AD-A191 056 DISCLINATION STRUCTURES IN CARBON AND GRAPHITE(U) 1/1
AEROSPACE CORP EL SEGUNDO CA MATERIALS SCIENCES LAB
J L WHITE 31 DEC 87 TR-0086(6720-01)-1 SD-TR-87-60
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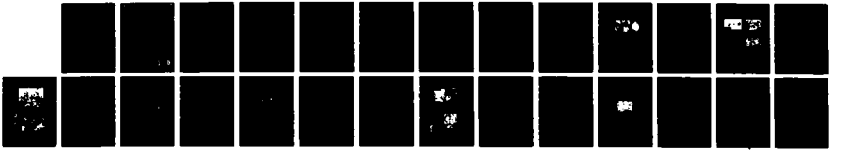

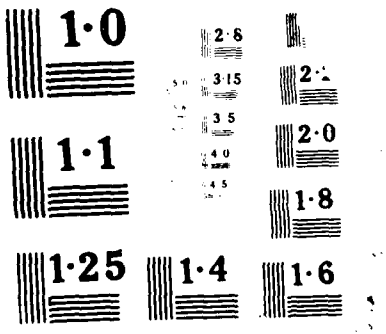
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REPORT SD-TR-87-60



# Disclination Structures in Carbon and Graphite

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31 December 1987

Prepared for

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AIR FORCE SYSTEMS COMMAND
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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245, under Contract No. F04701-85-C-0086 with the Space Division, P.O. Box 92960, Worldway Postal Center, Los Angeles, CA 90009-2960. It was reviewed and approved for The Aerospace Corporation by R. W. Fillers, Director, Materials Sciences Laboratory. Lt Donald Thoma, CLVT, was the Air Force project officer.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

# REPORT DOCUMENTATION PAGE

| | |
|---|---|
| 1a. REPORT SECURITY CLASSIFICATION<br>Unclassified | 1b. RESTRICTIVE MARKINGS<br>AD-A191 056 |
| 2a. SECURITY CLASSIFICATION AUTHORITY | 3. DISTRIBUTION / AVAILABILITY OF REPORT<br>Approved for public release; distribution unlimited. |
| 2b. DECLASSIFICATION / DOWNGRADING SCHEDULE | |
| 4. PERFORMING ORGANIZATION REPORT NUMBER(S)<br>TR-0086(6728-01)-1 | 5. MONITORING ORGANIZATION REPORT NUMBER(S)<br>SD-TR-87-60 |
| 6a. NAME OF PERFORMING ORGANIZATION<br>The Aerospace Corporation<br>Laboratory Operations<br>6b. OFFICE SYMBOL (*If applicable*) | 7a. NAME OF MONITORING ORGANIZATION<br>Space Division |
| 6c. ADDRESS (*City, State, and ZIP Code*)<br>E. Segundo, CA 90245 | 7b. ADDRESS (*City, State, and ZIP Code*)<br>Los Angeles Air Force Station<br>Los Angeles, CA 90009-2960 |
| 8a. NAME OF FUNDING / SPONSORING ORGANIZATION<br>8b. OFFICE SYMBOL (*If applicable*) | 9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER<br>F04701-85-C-0086 |
| 8c. ADDRESS (*City, State, and ZIP Code*) | 10. SOURCE OF FUNDING NUMBERS<br>PROGRAM ELEMENT NO / PROJECT NO / TASK NO / WORK UNIT ACCESSION NO |

11. TITLE (*Include Security Classification*)

Disclination Structures in Carbon and Graphite

12. PERSONAL AUTHOR(S)

White, Jack L.

| 13a. TYPE OF REPORT | 13b. TIME COVERED FROM ____ TO ____ | 14. DATE OF REPORT (*Year, Month, Day*) | 15. PAGE COUNT |
|---|---|---|---|
| | | 1987 December 31 | 21 |

16. SUPPLEMENTARY NOTATION

| 17. COSATI CODES | | |
|---|---|---|
| FIELD | GROUP | SUB-GROUP |
| | | |
| | | |

18. SUBJECT TERMS (*Continue on reverse if necessary and identify by block number*)

Mesophase, Coke, Carbon fiber, Oxidation, Disclination, Graphite, Carbonization, Stabilization, Liquid crystal, Pitch, Pyrolysis

19. ABSTRACT (*Continue on reverse if necessary and identify by block number*)

Carbon materials are structurally unique, owing to their relationship to liquid crystals. Pyrolysis of precursors that pass through a liquid crystalline (mesophase) state is the process by which most carbons form. The lamelliform morphologies that are locked in as the carbonaceous mesophase hardens lack grain boundaries but possess disclinations as their most prominent structural feature. Practical materials, ranging in value from petroleum coke to mesophase carbon fiber, form while the mesophase undergoes deformation, and the disclinations can react extensively before they are entrapped by hardening. Thus, most carbons and graphites may be regarded as mesophase fossils with disclination-dominated microstructures that vary with the nature and extent of deformation and with the time allowed for the disclinations to react and relax before hardening.

| 20. DISTRIBUTION / AVAILABILITY OF ABSTRACT | 21. ABSTRACT SECURITY CLASSIFICATION |
|---|---|
| ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS | Unclassified |
| 22a. NAME OF RESPONSIBLE INDIVIDUAL | 22b. TELEPHONE (*Include Area Code*) / 22c. OFFICE SYMBOL |

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

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PREFACE

We thank the Office of Naval Research for supporting the preparation of this paper, which includes selected aspects of work supported by the Space Division of the U.S. Air Force and the Naval Surface Weapons Center. We also thank several coworkers who have contributed in significant ways: J. E. Zimmer, M. Buechler, C. B. Ng, G. W. Henderson, and P. M. Sheaffer.

This paper was given at the Third International Conference on Ultrastructure Processing of Ceramics, Glasses, and Composites held in San Diego, California, 24-27 February 1987.

CONTENTS

FIGURES

# I. INTRODUCTION

Most carbon and graphite materials originate in the pyrolysis of organic precursors derived from oil or coal, and the critical stage in establishing the layered molecular architecture is the transition through the liquid-crystalline state known as the carbonaceous mesophase. The extensive "chicken-wire" molecules formed by aromatic polymerization are stiff and strong in their layer planes, but the weak bonding between adjacent parallel layers permits turbostratic stacking (the absence of crystalline registry between layers). As illustrated by Fig. 1, the layers can bend, splay, and twist to form microstructures quite different from those of other ceramic materials.

Various processes have been developed to form carbon into filaments.[1] When those processes also produce strong preferred orientations of graphitic layers parallel to the filament, the tensile moduli may exceed those of all competitive fibers. Although the most commonly used fibers today are produced by spinning and carbonizing polyacrylonitrile (PAN), the highest tensile moduli are attained in fibers spun from pitch in the mesophase (liquid crystalline) state. Both fiber types represent solutions to the basic microstructural problem of how to realize the strength and stiffness of the two-dimensional graphitic layer in a three-dimensional body.

Mesophase carbon fibers exemplify the manipulation of basic mesophase mechanisms to form favorable microstructure in carbon products.[2] The structural details generally are too fine to be resolved by the polarized-light techniques that are useful for such mesophase products as petroleum coke. However, tensile fracture of the high-modulus fibers occurs with extensive shear, and the resulting serrated fracture surfaces provide good structural definition for SEM observations. The filaments in Fig. 2 include three basic fiber morphologies, all of which can be sketched plausibly in terms of mesophase disclinations.[3]

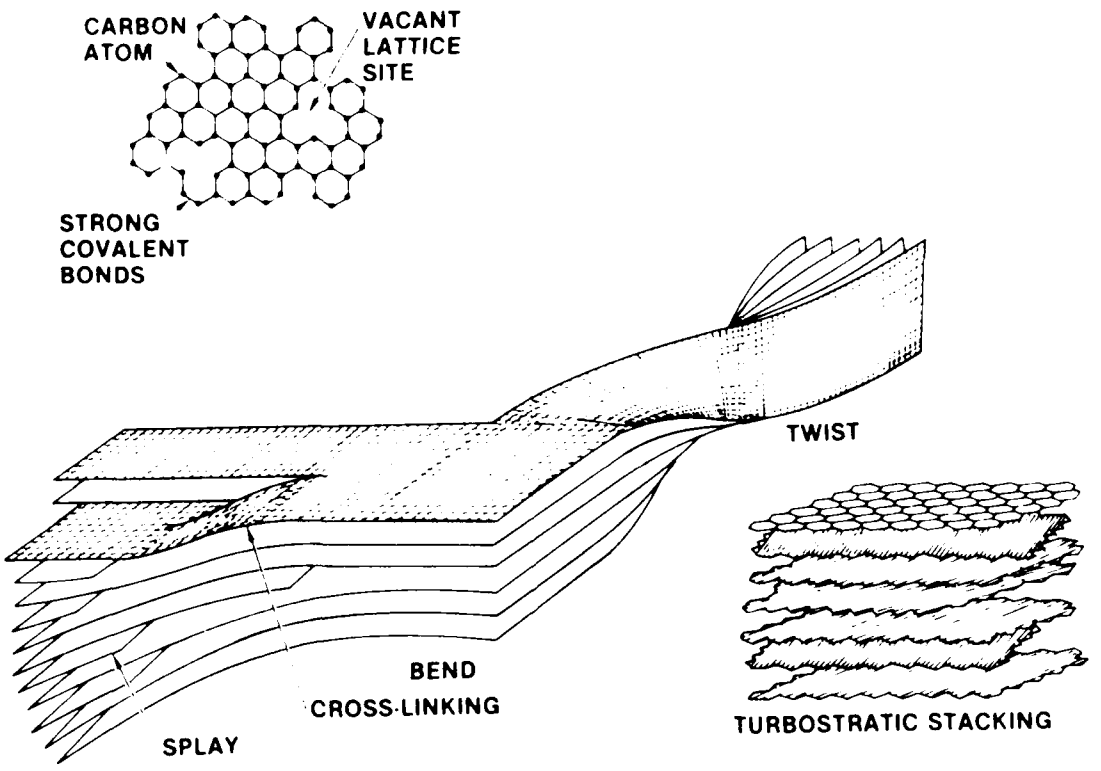



Fig. 1. Lamelliform morphology of carbon and graphitic materials.

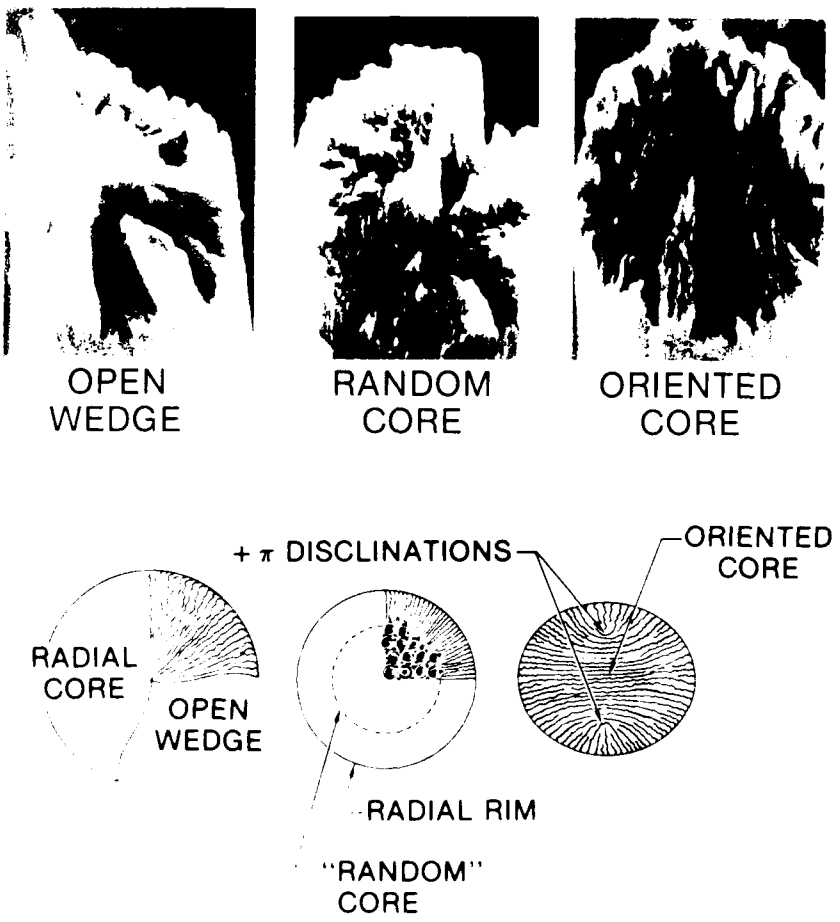
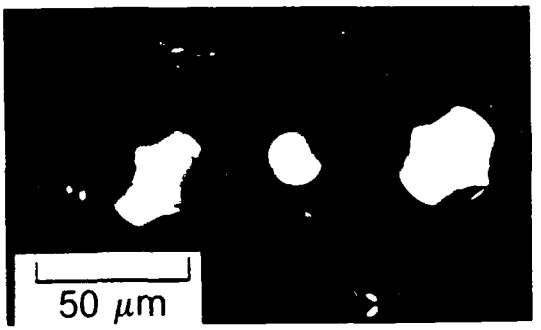



Fig. 2. Mesophase carbon fiber. Above: Tensile fracture surfaces for three types of high-modulus fibers spun from mesophase pitch. Below: Structural models for these fibers. From Ref. 3.

## II. THE CARBONACEOUS MESOPHASE

The polarized-light micrographs and layer morphologies of mesophase spherules formed in a pyrolyzed pitch (Fig. 3), although now familiar to carbon technologists, may seem strange to metallurgists or ceramists. The three-dimensional layer morphology also seemed unlikely to G. H. Taylor, who first tentatively proposed that structure in 1961.[5] In subsequent work with J. D. Brooks,[6] he applied selected-area electron diffraction to confirm what has come to be known as the Brooks and Taylor structure. Those pioneering workers then went on to demonstrate that the mesophase transformation is the basic mechanism determining both the microstructure and graphitizability of carbon materials produced by the pyrolysis of organic liquids.[7]

The carbonaceous mesophase usually appears in the pyrolysis of tars or other organic precursors at about 400°C, at which point polymerization reactions produce large, flat molecules with weights of 500 amu or higher. The molecules have widely varying size and structural detail, but their parallel alignment establishes a discotic nematic order similar to that of conventional liquid crystals for which the structural units are rods rather than discs. Mesophase formation may be viewed as a liquid-state ordering transformation, but the molecules align only approximately parallel, and bend, splay, and twist deformations are accommodated with little strain energy.[8] Soon after the mesophase spherules appear, bulk mesophase begins to form by the coalescence process illustrated in Fig. 4. The resulting lamelliform morphology extends throughout the body without interruption by grain boundaries.



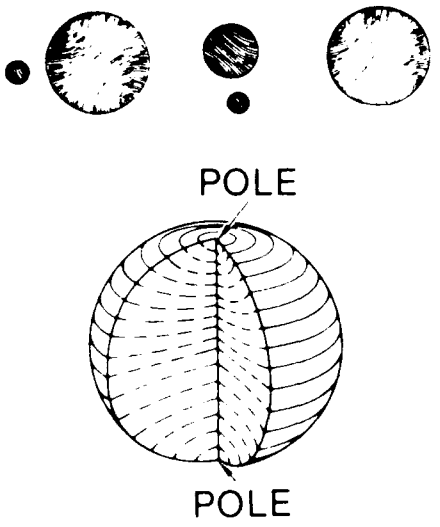




Fig. 3. Brooks and Taylor morphology of mesophase spherules; from Ref. 4.

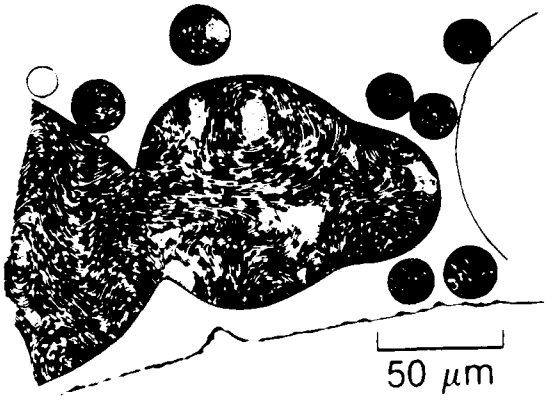




Fig. 4. Coalescence of spherules to form bulk mesophase; from Ref. 4.

## III. MESOPHASE MORPHOLOGY AND DISCLINATION STRUCTURES

In bulk mesophase observed by crossed polarizers (Fig. 5), nodes and crosses appear as prominent features of the polarized light extinction contours. The nodes and crosses rotate either with or against the plane of polarization when the plane of polarization (or the microscope stage) is rotated, but their centers remain fixed at specific points on the polished surface of the bulk mesophase. When the layer orientations are mapped, as in Fig. 6, the nodes and crosses correspond to disclinations of the same type as those observed in nematic liquid crystals.[10] They are essentially layer-stacking discontinuities that result from the ease of bend, splay, and twist in the liquid crystal.[11]

Disclinations are rare in ordinary crystalline materials. Figure 7 indicates the reason: The distortions at the core of a crystal disclination are so large that disclinations are prohibited from forming, except by entrapment mechanisms, such as the hardening of a liquid crystal. Figure 7 also illustrates how a Nabarro circuit (analogous to a Burgers circuit for a crystal dislocation) can be used to define the rotational strength of a disclination.[12]

Models of the wedge and twist disclinations commonly found in the carbonaceous mesophase are sketched in Fig. 8. Under observation by polarized light, the $\pm\pi$ disclinations appear as nodes and the $\pm 2\pi$ disclinations appear as crosses. The twist disclination represents the case in which the disclination line runs normal to the Nabarro rotation vector.

Knowing the way mesophase behaves when in contact with carbon fiber is important to the fabrication of carbon-fiber-reinforced carbon-matrix composite materials. Mesophase layers normally align parallel to the substrate filaments to produce a sheath effect (Fig. 9) that dominates the formation of microstructure in the matrix.[13] The matrix disclinations within a fiber bundle can thus be readily predicted from the geometry of filaments surrounding each matrix channel. A sketch of a $-2\pi$ disclination is included in Fig. 9 to show that the cores of $\pm 2\pi$ disclinations need not be discontinuous as


Fig. 5. Nodes and crosses observed by crossed polarizers on polished section of bulk mesophase; from Ref. 9.

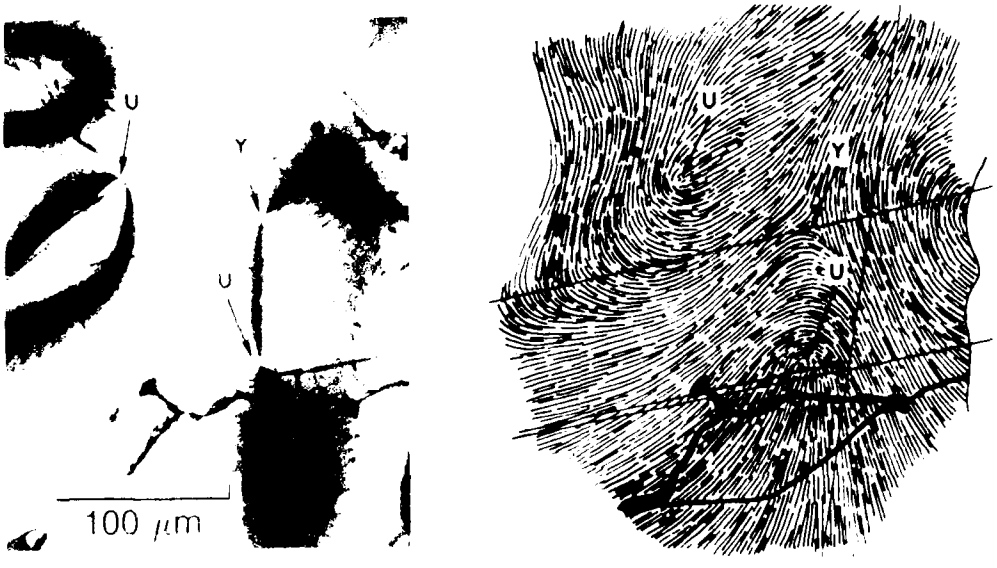



Fig. 6. Mapping disclinations on a polished section of bulk mesophase; from Ref. 10.

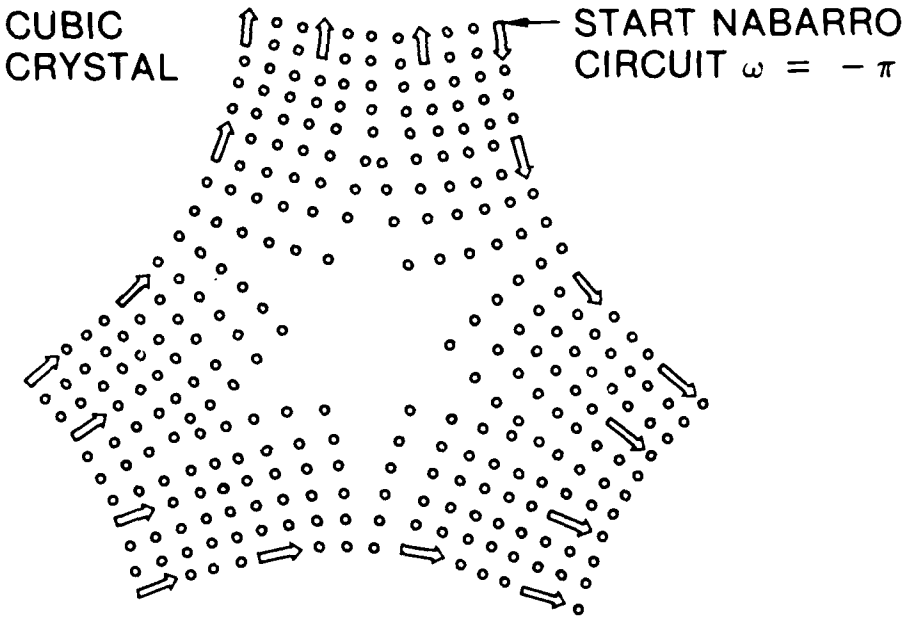



Fig. 7. Disclination of -π rotational strength in a simple cubic crystal. Nabarro vector measures rotation of lattice vector in circuit around disclination; from Ref. 3.

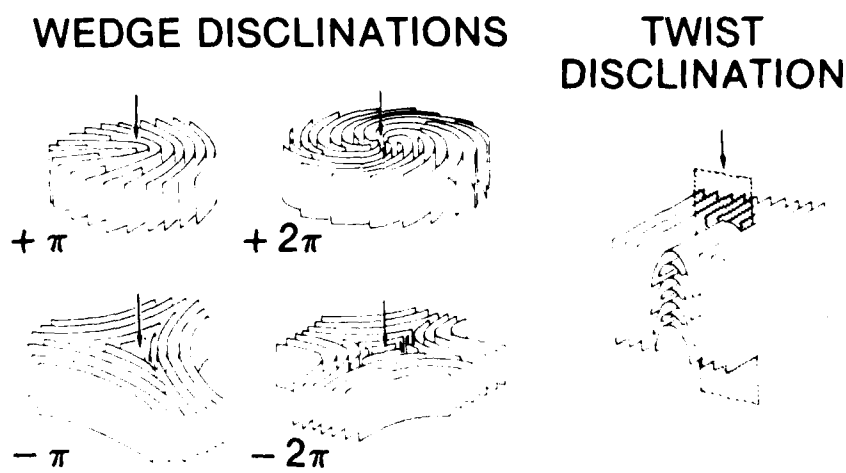



Fig. 8. Schematic models for the wedge and twist disclinations of the carbonaceous mesophase; from Ref. 3.

sketched in Fig. 8; instead, the layers of the core tilt to form a saddlelike configuration.

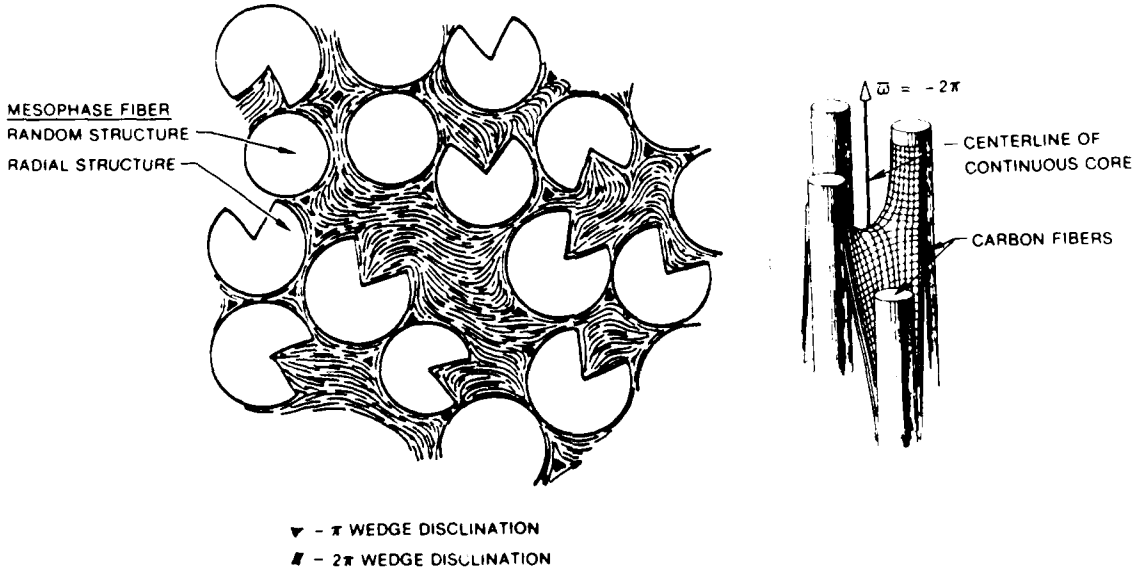



Fig. 9. Mesophase alignment within a fiber bundle; from Ref. 13.

## IV. MESOPHASE DEFORMATION AND DISCLINATION REACTIONS

The presentation of this paper included a seven-minute film prepared by hot-stage microscopy, to demonstrate the dynamic aspects of mesophase behavior. The film, made by M. Buechler and C. B. Ng of our Materials Sciences Laboratory, summarizes their observations of mesophase coalescence, disclination reactions, and mesophase deformation in the pyrolysis of a petroleum pitch (Ashland A240).[14,15] [The film is available at cost ($25), in either 16-mm film or VHS videocassette, by application to the address given on the cover.] The various structural phenomena appear with good clarity at a free surface because the mesophase layers preferentially stand perpendicular to the surface.

Over sixty years ago, Friedel[16] showed that all possible reactions between $\pm\pi$ and $\pm 2\pi$ disclinations can occur in conventional nematic liquid crystals; they also occur in the carbonaceous mesophase, including:

Annihilation and formation reactions, $(\pm 2\pi) + (\mp 2\pi) \rightleftharpoons 0$

Combination and dissociation reactions, $(\pm\pi) + (\pm\pi) \rightleftharpoons (\pm 2\pi)$

As pyrolysis proceeds, the viscosity rises and the disclination reactions slow well before the mesophase hardens to a coke. The spatial geometry of reactions between disclinations of different order, e.g., $(\pm\pi) + (\mp 2\pi) \rightleftharpoons (\mp\pi)$, has been studied by sequentially sectioning quenched mesophase.[17] Such reactions consist of three disclinations meeting at a reaction point whose direction of motion determines the direction of the reaction (Fig. 10).

Mesophase flow is fundamental to mesophase-fiber spinning and needle-coke formation as well as to the disclination-structure formation within the products. Mesophase rods can be drawn by uniaxial deformation to produce fibrous morphologies consisting of nearly pure wedge disclination lines running parallel to the draw direction. Biaxial deformation, as experienced by the wall of an expanding bubble, produces lamellar morphologies with folded mesophase layers;[9] as sketched in Fig. 11, the folds are bounded by disclinations that vary from pure twist to pure wedge. If the depicted disclination loop subsequently undergoes extension, it can deform to a pair of closely

spaced wedge disclinations of opposite sign, poised for an annihilation reaction if the viscosity has not risen too high.

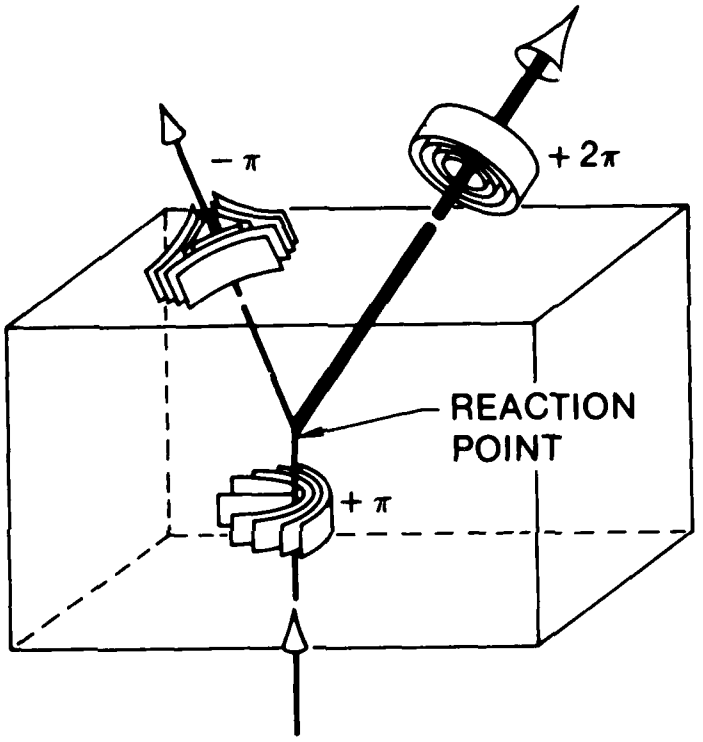



Fig. 10. Spatial sketch of a disclination reaction; from Ref. 3.

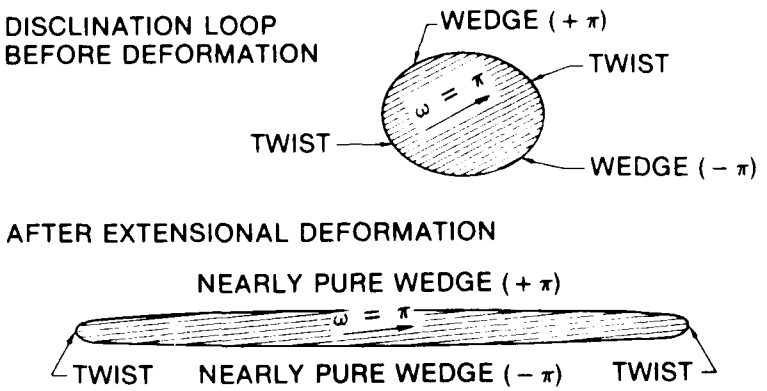


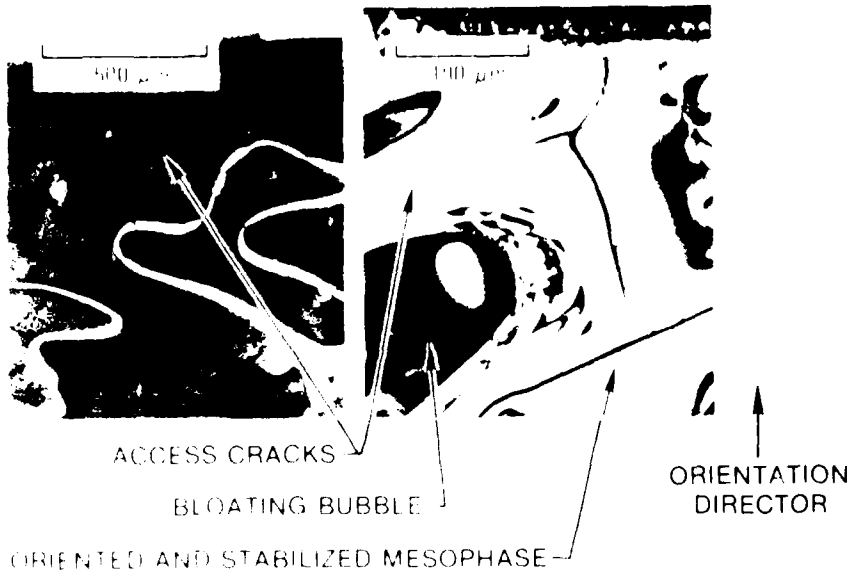

Fig. 11. A folded region in bulk mesophase can be represented as a disclination loop. Uniaxial deformation alters the spacing and character of the disclinations; from Ref. 3.

## V. STABILIZATION OF DISCLINATION ARRAYS

To preserve a given disclination array, such as the wedge disclinations of a spun mesophase fiber, in a graphitized body, the microstructure must be stabilized so that shape changes and disclination reactions will not occur during the carbonization required to convert the mesophase to graphite. Mesophase fibers with ~10-μm diameters are stabilized by diffusing oxygen into the filaments to immobilize the mesophase by cross-linking; an oxygen content of 8 wt% has been reported sufficient to stabilize fiber spun from a petroleum-based mesophase pitch.[13] To learn the extent to which oxidation can be used to stabilize disclination structures in bulk mesophase, we have measured the effective stabilization depths in mesophase bodies with well-defined microstructures.[14]

Our aim was to prepare oriented mesophase bodies by applying a magnetic field during pyrolysis or by extruding and drawing a mesophase pitch, to oxidize the bodies below the softening point, and then to carbonize and observe the depth to which the original microstructure was retained. In the results of a stabilization experiment on a magnetically oriented mesophase plate (Fig. 12), essentially a disclination-free single liquid crystal,[20] the oriented ribs along the cracks in the carbonized specimen evidence the microstructure to be stabilized to a depth of 17 μm from any crack with access to the oxygen atmosphere.

In similar oxidation and carbonization experiments on drawn mesophase rods, illustrated by Fig. 13, the depth of stabilization was indicated by coarsening of the fibrous microstructure. As with the magnetically oriented mesophase, oxidation proceeded to equivalent depths from the free surface and from cracks with access to oxygen. Insufficiently oxidized mesophase melted and was often driven from within the oxidized casing by the pressure of pyrolysis gases. In all mesophase specimens, the oxidation process showed strong throwing power along the shrinkage cracks that result from anisotropic thermal expansion.




[illegible] mesophase: (a) [illegible] The orientation [illegible] lies in the plane of [illegible]



[illegible] mesophase [illegible]

We recently extended our stabilization experiments to mesophase-impregnated fiber composites for which the mismatch in thermal expansion between fiber and mesophase forces an extensive network of shrinkage cracks.[21] Composite panels as thick as 8 mm have been stabilized. Although oxidation levels higher than 15 wt% were involved, the oxygen was evolved from the matrix during carbonization without damage to fiber or matrix and without loss in net carbon yield.

## VI. DISCUSSION

Our understanding of the mesophase and its microstructures is still rudimentary, but observations of deformation effects and disclination reactions are sufficient to suggest how the quite different fiber morphologies of Fig. 2 originate. The extensive draw involved in filament spinning must produce a dense array of wedge disclinations lying within easy reaction distance. The extent to which reactions occur depends on viscosity and rate of cooling after spinning. Under conditions of low viscosity and gentle quench, disclination annihilation reactions may proceed to completion, leaving a single $+2\pi$ wedge disclination at the center of a radial filament; upon carbonization, the characteristic open wedge is formed by mesophase shrinkage perpendicular to the layers. The random-core filament results from higher mesophase viscosity and more severe quenching to trap an appreciable number of disclinations to form the random core. The oval filament, then, represents an intermediate state of disclination reaction that leaves two $+\pi$ wedge disclinations separated by an oriented core; the oval shape results, again, from anisotropic mesophase shrinkage during carbonization.

The essential elements of a mesophase technology can now be perceived for the preparation of carbon materials having controlled disclination arrays. Following the path developed empirically for mesophase carbon fibers, that technology consists of manipulating the mesophase in its plastic state to form desired disclination structures, then oxidizing the mesophase to stabilize the shape and microstructure for carbonization. How far such paths can be pursued to produce useful products--pencil leads, to offer a very practical example--depends critically on questions of mesophase behavior that have not yet received careful scrutiny; for example, What determines the formation of distributed shrinkage cracks instead of massive fractures when a mesophase body of complex microstructure is carbonized?

This discussion of disclination structures has been developed entirely in terms of the carbonaceous mesophase. Disclinations must also be anticipated in carbons formed by processes other than the mesophase transformation, e.g.,

from the glass-forming precursors used to produce PAN-based carbon fibers. From extensive studies by high-resolution electron microscopy, Oberlin and coworkers[22] have proposed the disclinated model of Fig. 14 for PAN-based carbon fiber. What distinguishes that model from the mesophase carbon fibers are the close spacing of disclinations and the fine elongated porosity that appears to limit those fibers to lower density levels.

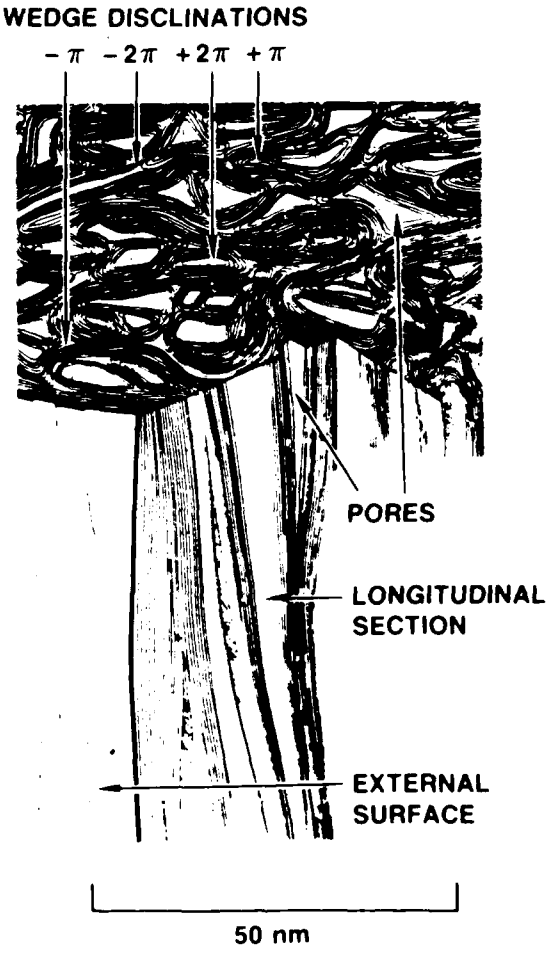



Fig. 14. Structural model for PAN-based carbon fiber; after Guigon et al. (Ref. 22).

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Computer Science Laboratory: Program verification, program translation, performance-sensitive system design, distributed architectures for spaceborne computers, fault-tolerant computer systems, artificial intelligence, microelectronics applications, communication protocols, and computer security.

Electronics Research Laboratory: Microelectronics, solid-state device physics, compound semiconductors, radiation hardening; electro-optics, quantum electronics, solid-state lasers, optical propagation and communications; microwave semiconductor devices, microwave/millimeter wave measurements, diagnostics and radiometry, microwave/millimeter wave thermionic devices, atomic time and frequency standards; antennas, rf systems, electromagnetic propagation phenomena, space communication systems.

Materials Sciences Laboratory: Development of new materials: metals, alloys, ceramics, polymers and their composites, and new forms of carbon; nondestructive evaluation, component failure analysis and reliability; fracture mechanics and stress corrosion; analysis and evaluation of materials at cryogenic and elevated temperatures as well as in space and enemy-induced environments.

Space Sciences Laboratory: Magnetospheric, auroral and cosmic ray physics, wave-particle interactions, magnetospheric plasma waves, atmospheric and ionospheric physics, density and composition of the upper atmosphere, remote sensing using atmospheric radiation, solar physics, infrared astronomy, infrared signature analysis; effects of solar activity, magnetic storms and nuclear explosions on the earth's atmosphere, ionosphere and magnetosphere; effects of electromagnetic and particulate radiations on space systems, space instrumentation.

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